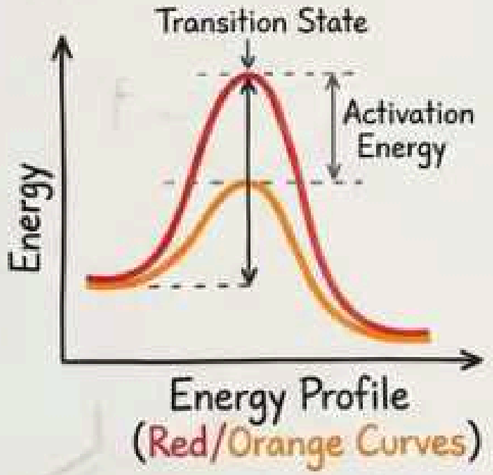
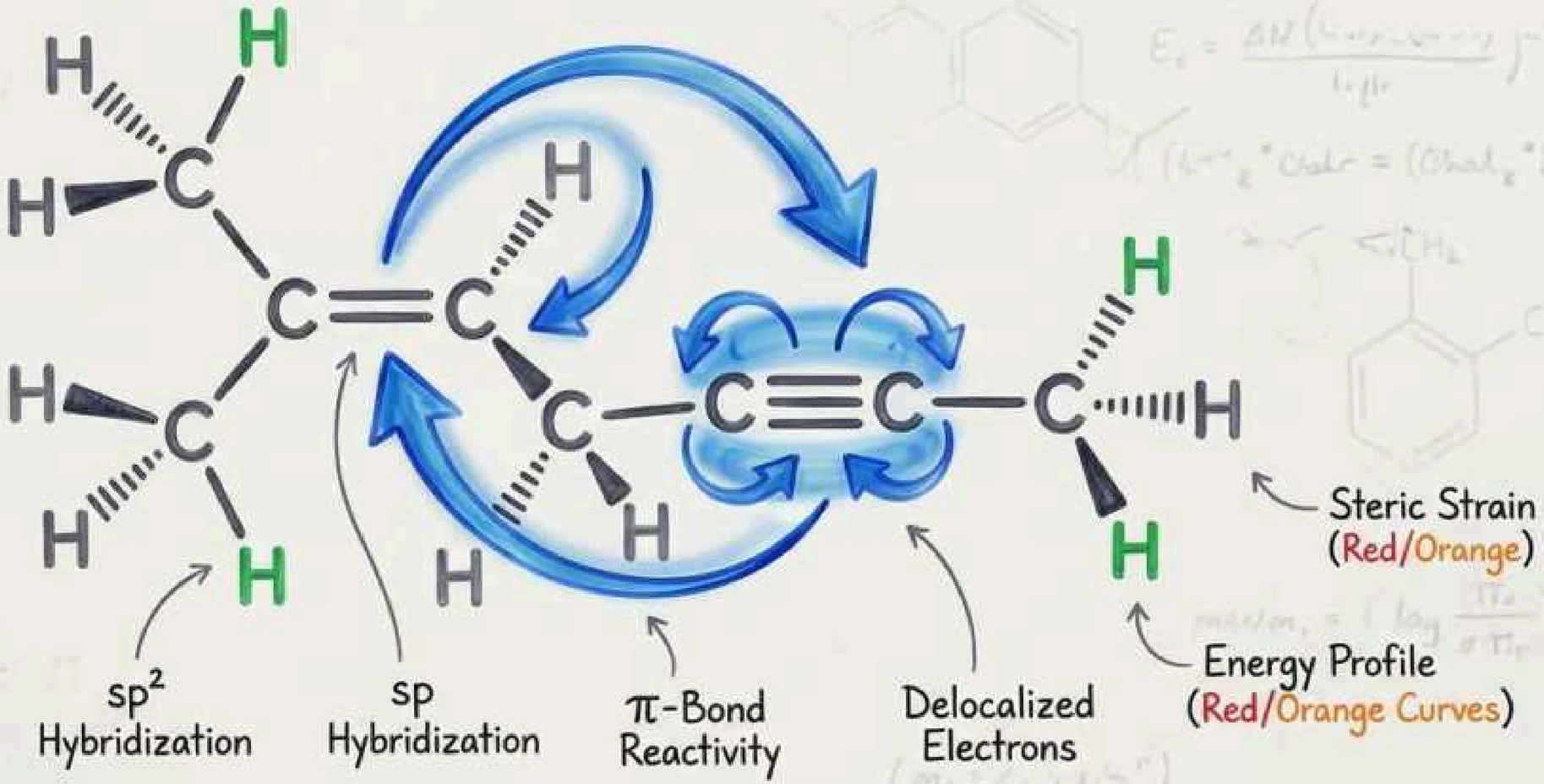
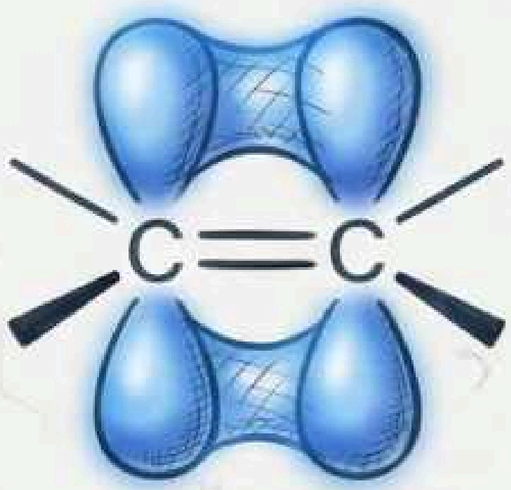
Alkenes and Alkynes

Structure, Flow, and Stability.

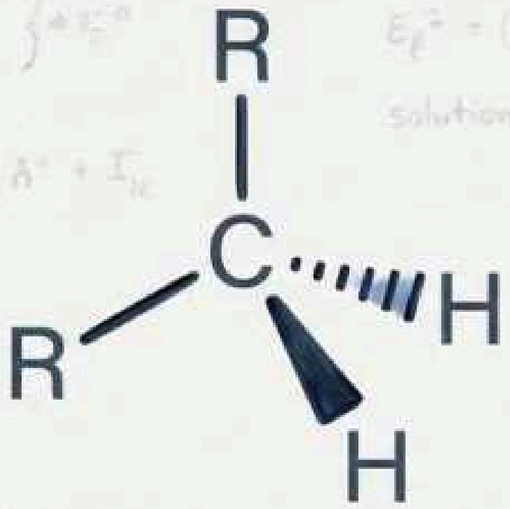




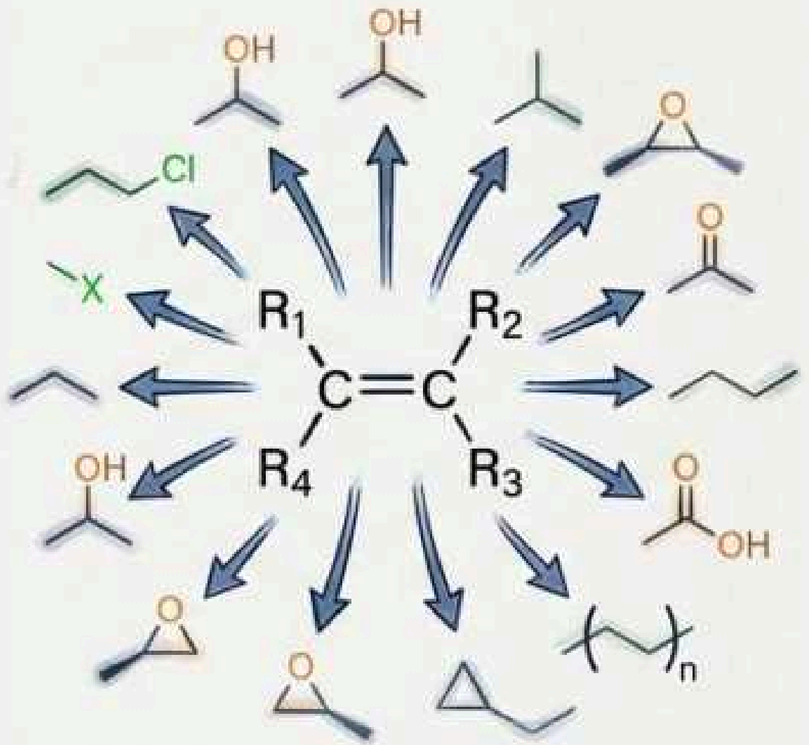
Three questions organize this lecture



1. Why are double and triple bonds so reactive?



2. How do reagents add (orientation & stereochemistry)?

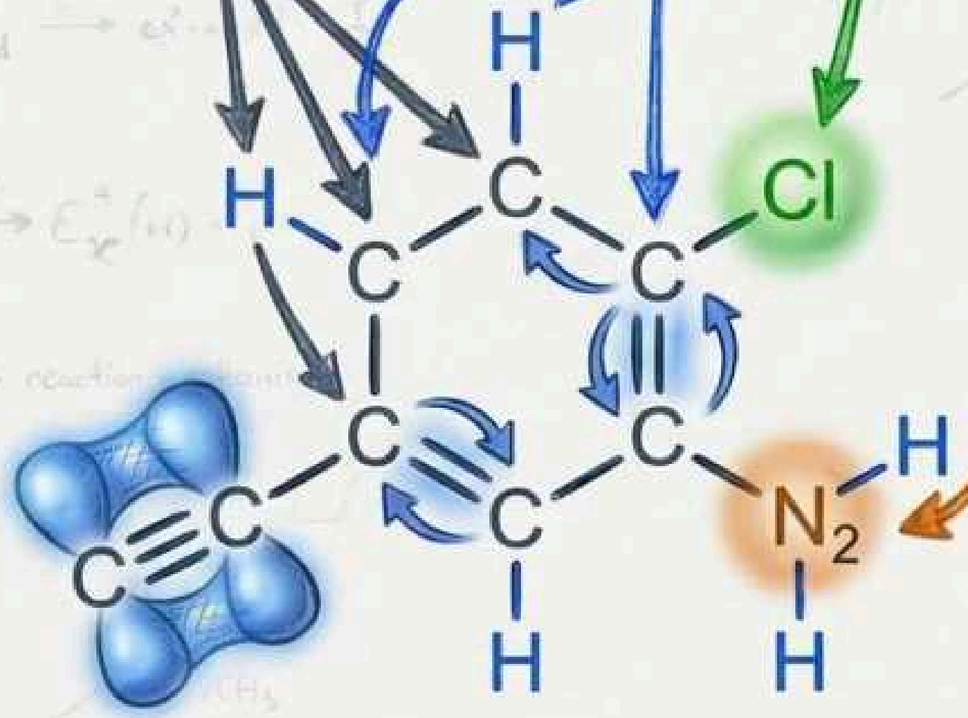


3. How does one alkene become a dozen compounds?

Alkenes are the workhorses of organic synthesis—teaching the central logic of mechanism.

The degree of unsaturation counts rings and pi bonds

$$\text{DoU} = C + 1 - \frac{(H + X)}{2} + \frac{N}{2}$$

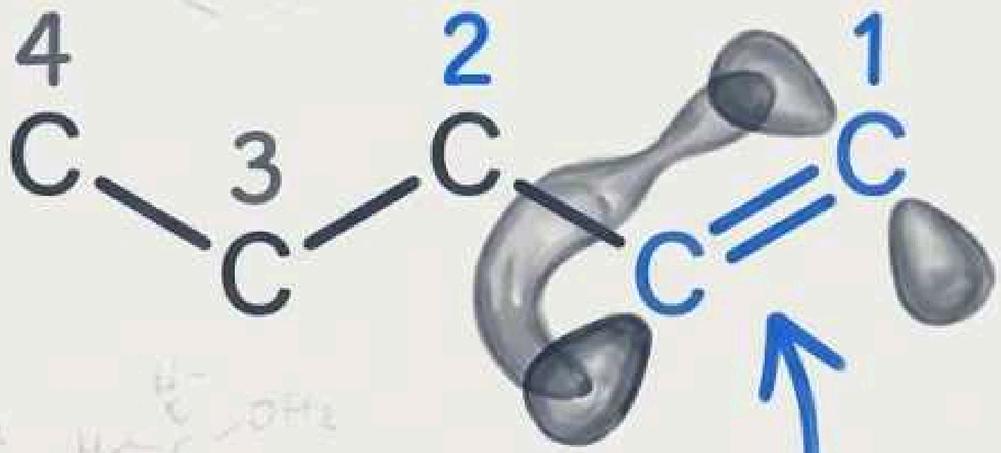


Unsaturated: Holding fewer hydrogens than the corresponding alkane.

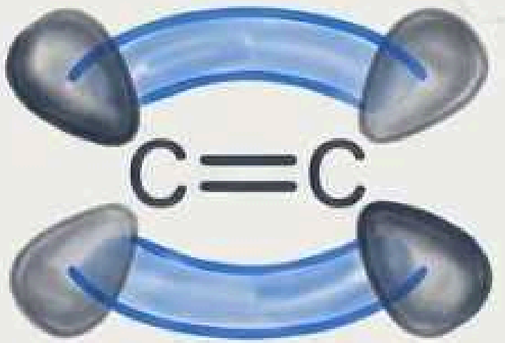
Nomenclature follows the alkane scheme with specific endings

¶ 6.3

- -ene (double bond)
- -yne (triple bond)



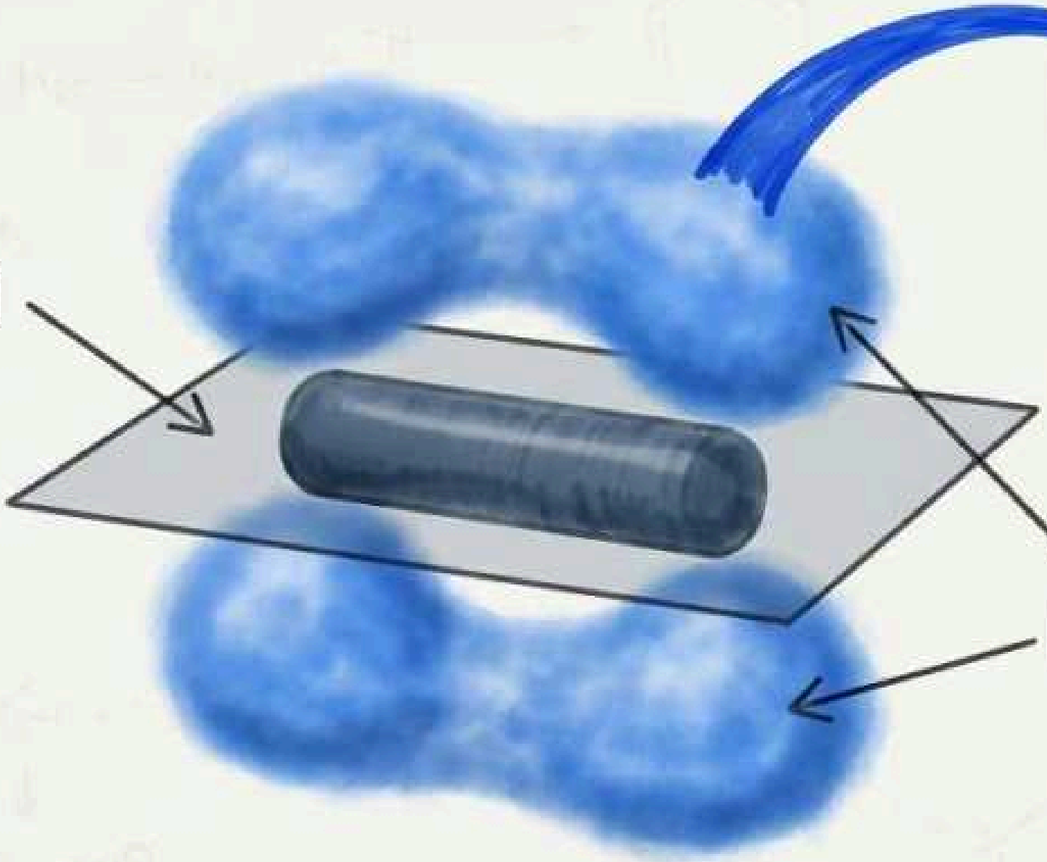
1-butene 1



Ethene (Ethylene):
The simplest alkene and the most produced organic chemical in the world.

¶ 6.4

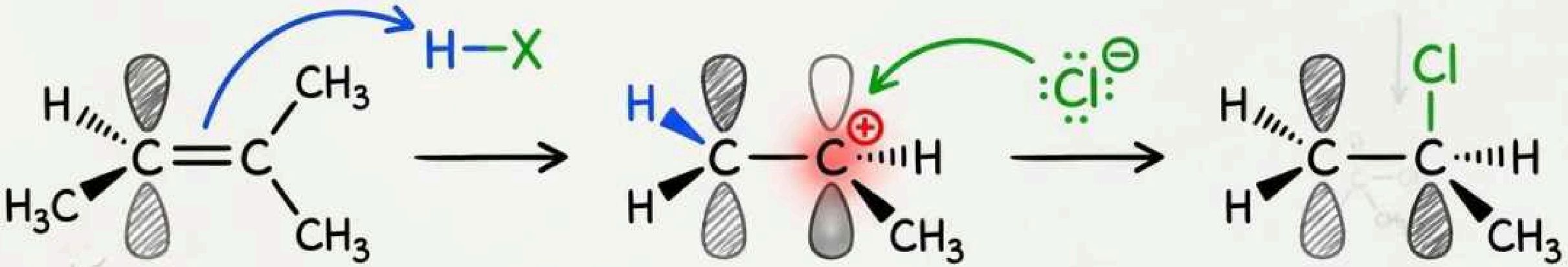
Carbon-carbon double and triple bonds are inherently reactive nucleophiles



Addition Reaction: 1 Pi Bond Breaks → 2 New Sigma Bonds Form
(The opposite of elimination)

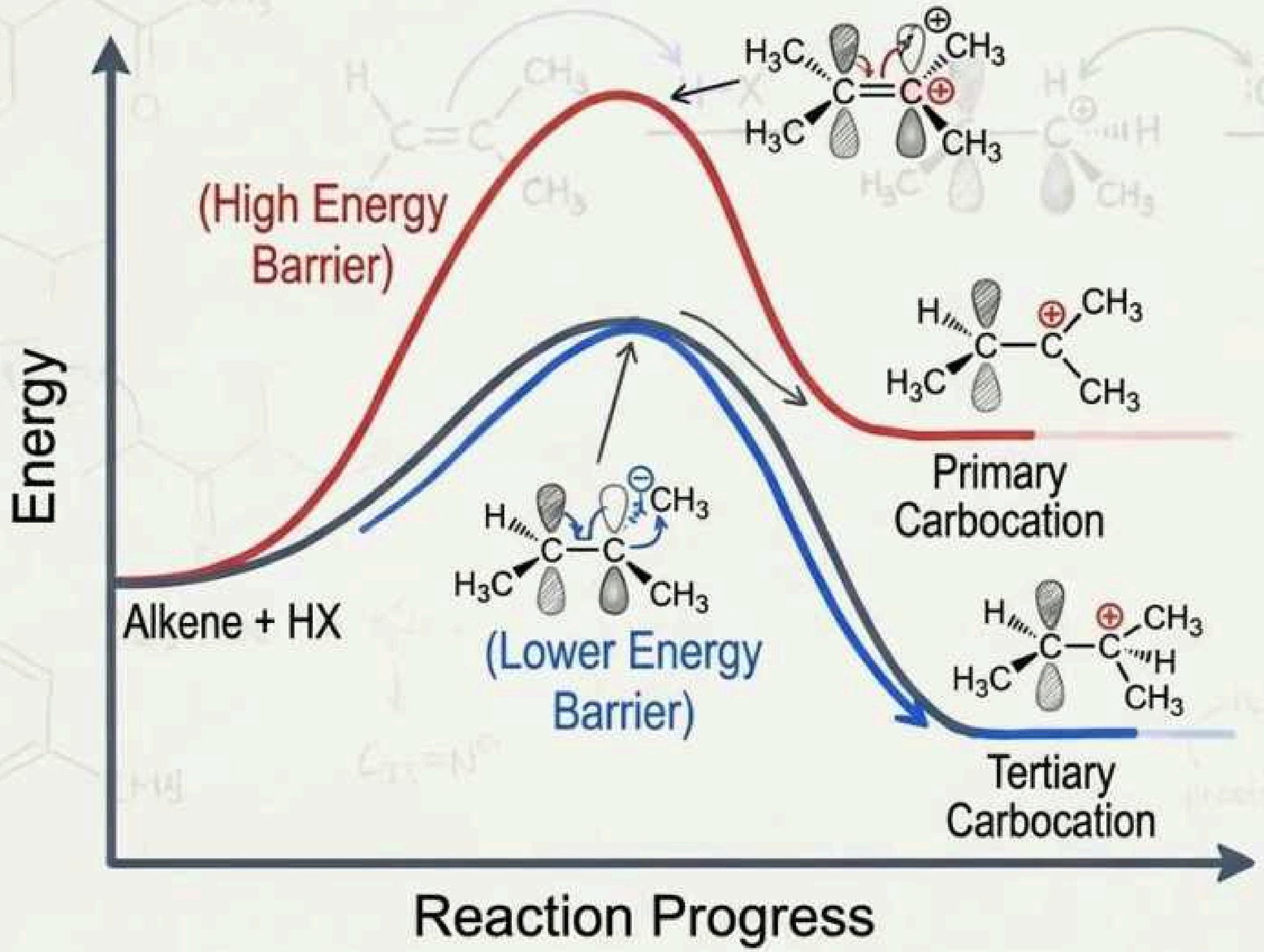
Hydrogen halides add across the bond following Markovnikov's observation

Observed by Vladimir Markovnikov, 1869.



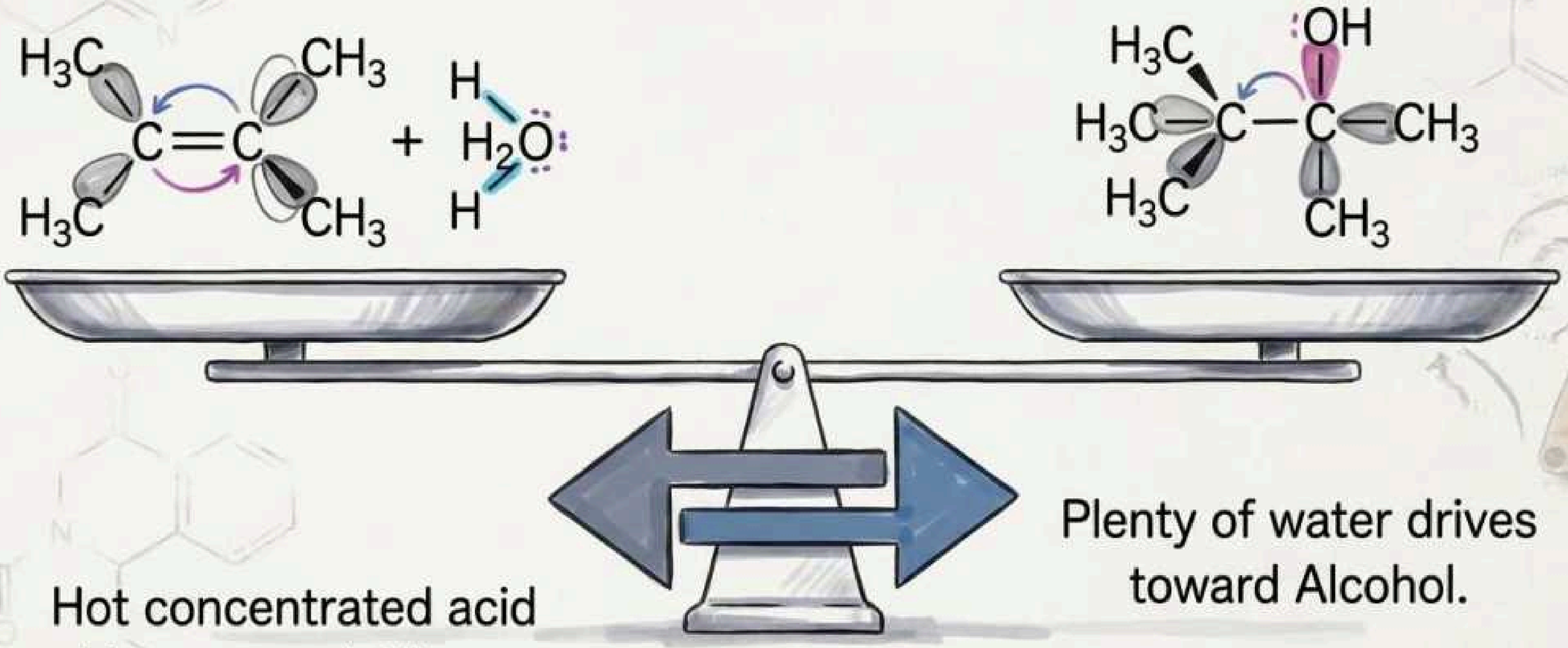
Hydrogen goes to the carbon with more hydrogens.
Halogen goes to the more substituted carbon.

Hammond's postulate reveals Markovnikov's rule is a stability rule

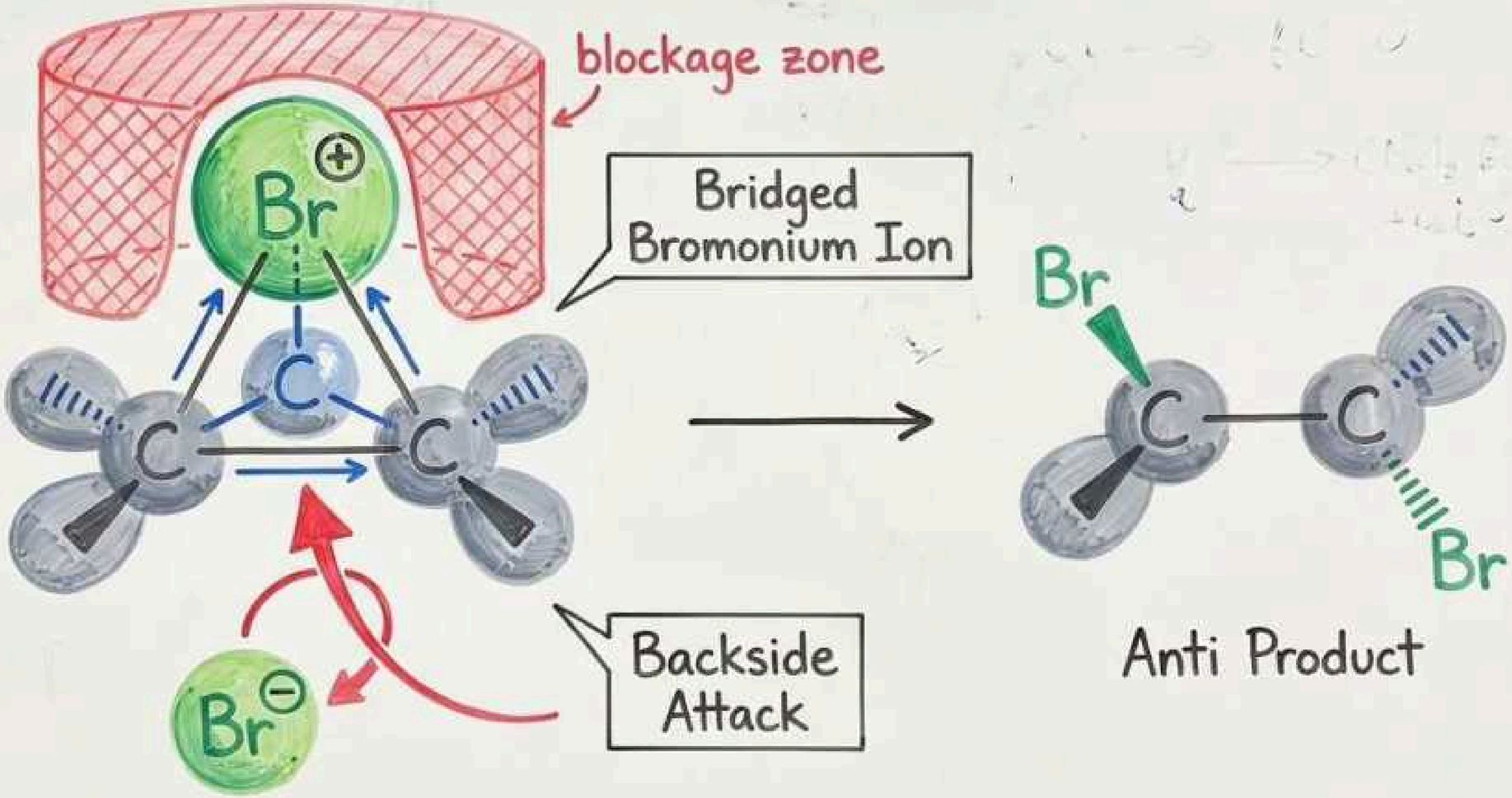


Caution: Carbocations can rearrange before the halide arrives, leading to unexpected structures.

Acid-catalyzed hydration establishes a reversible equilibrium



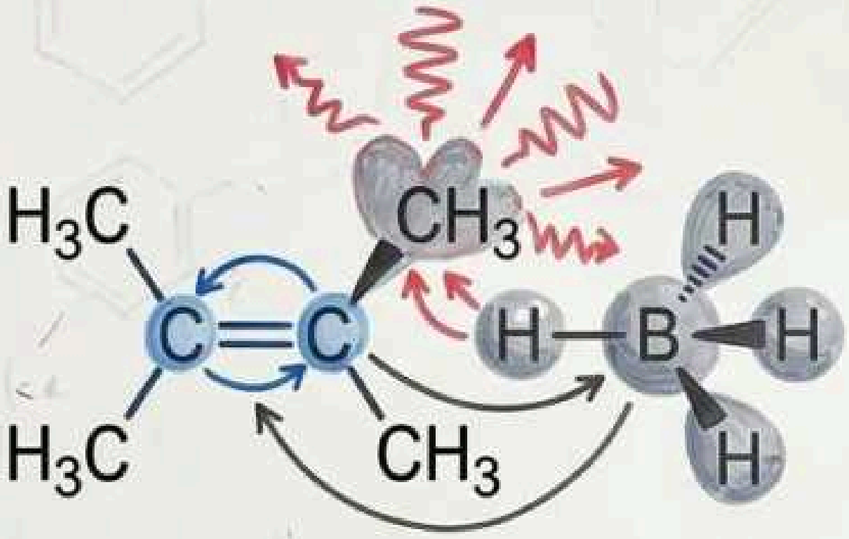
Halogenation proceeds through a bridged intermediate to enforce anti addition



Reaction in water gives a bromohydrin (hydroxyl + bromine on neighboring carbons).

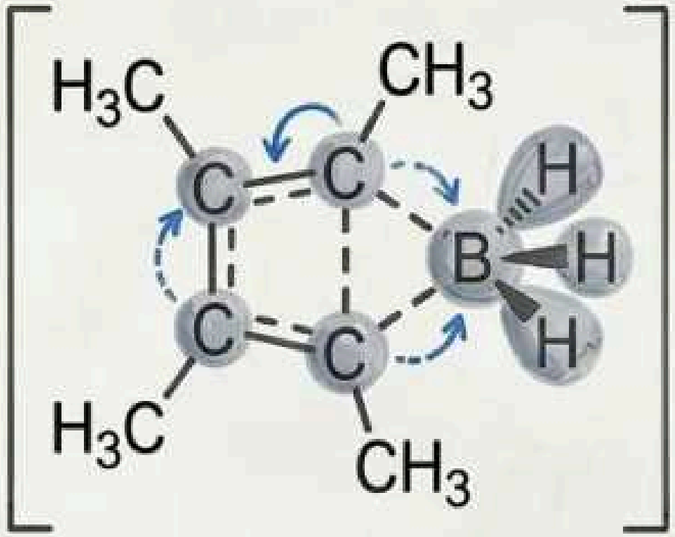
Hydroboration achieves anti-Markovnikov orientation through syn addition

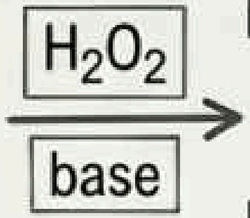
Steric-Directed Approach

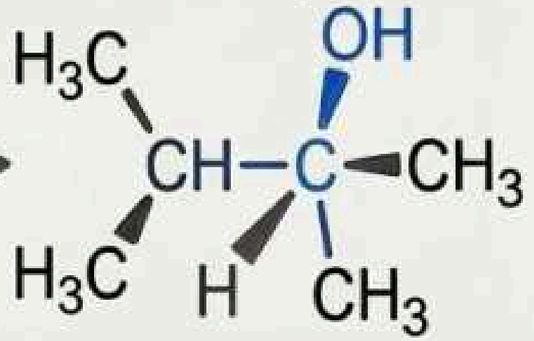


Bulky Boron atom aligns with less crowded terminal carbon due to steric repulsion.

Syn Transition State (Concerted Addition)





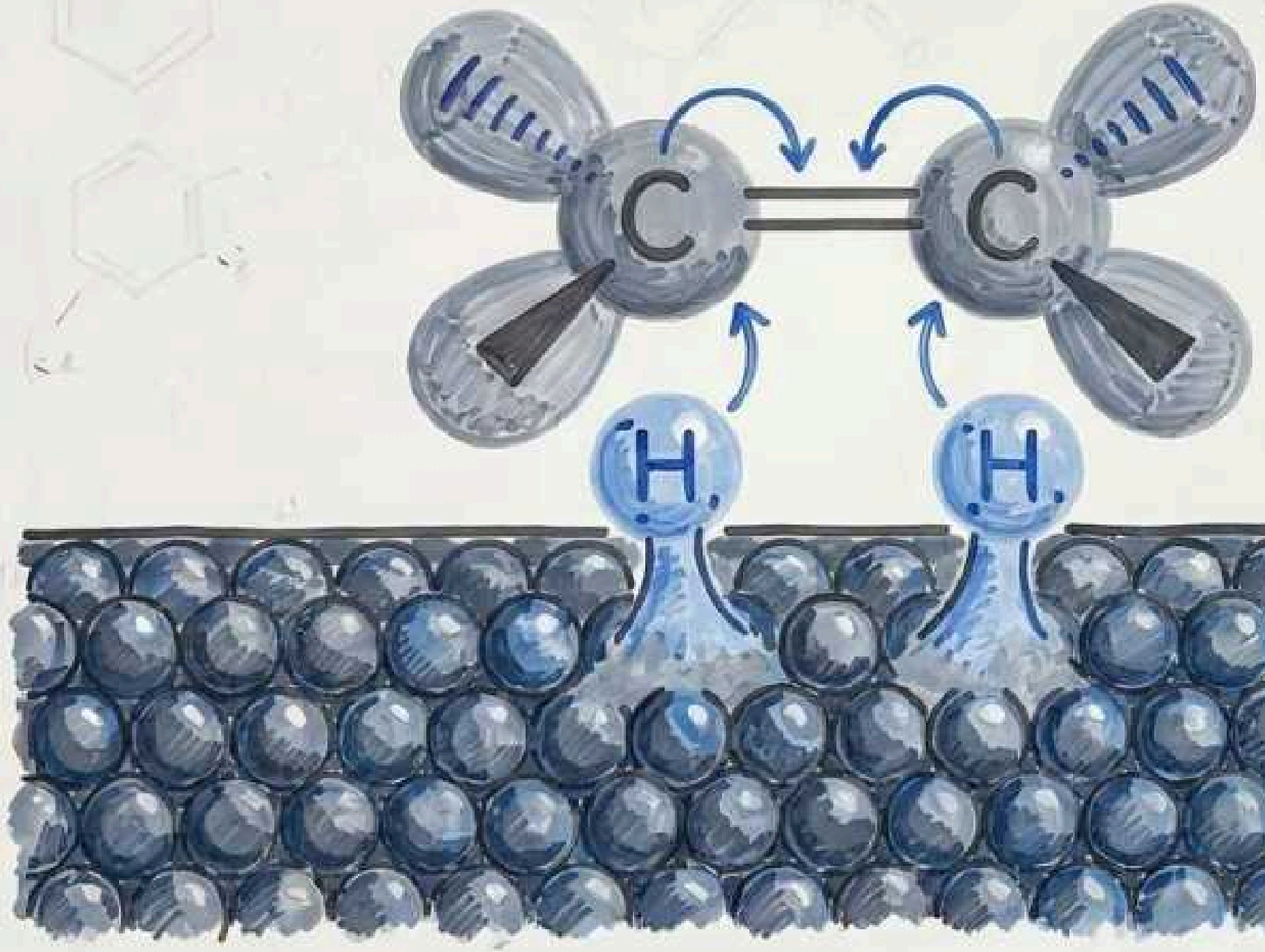


Anti-Markovnikov Alcohol (Syn Addition)



Discovered by Herbert C. Brown (shared 1979 Nobel Prize with Georg Wittig).

Catalytic hydrogenation delivers hydrogen atoms to the same face

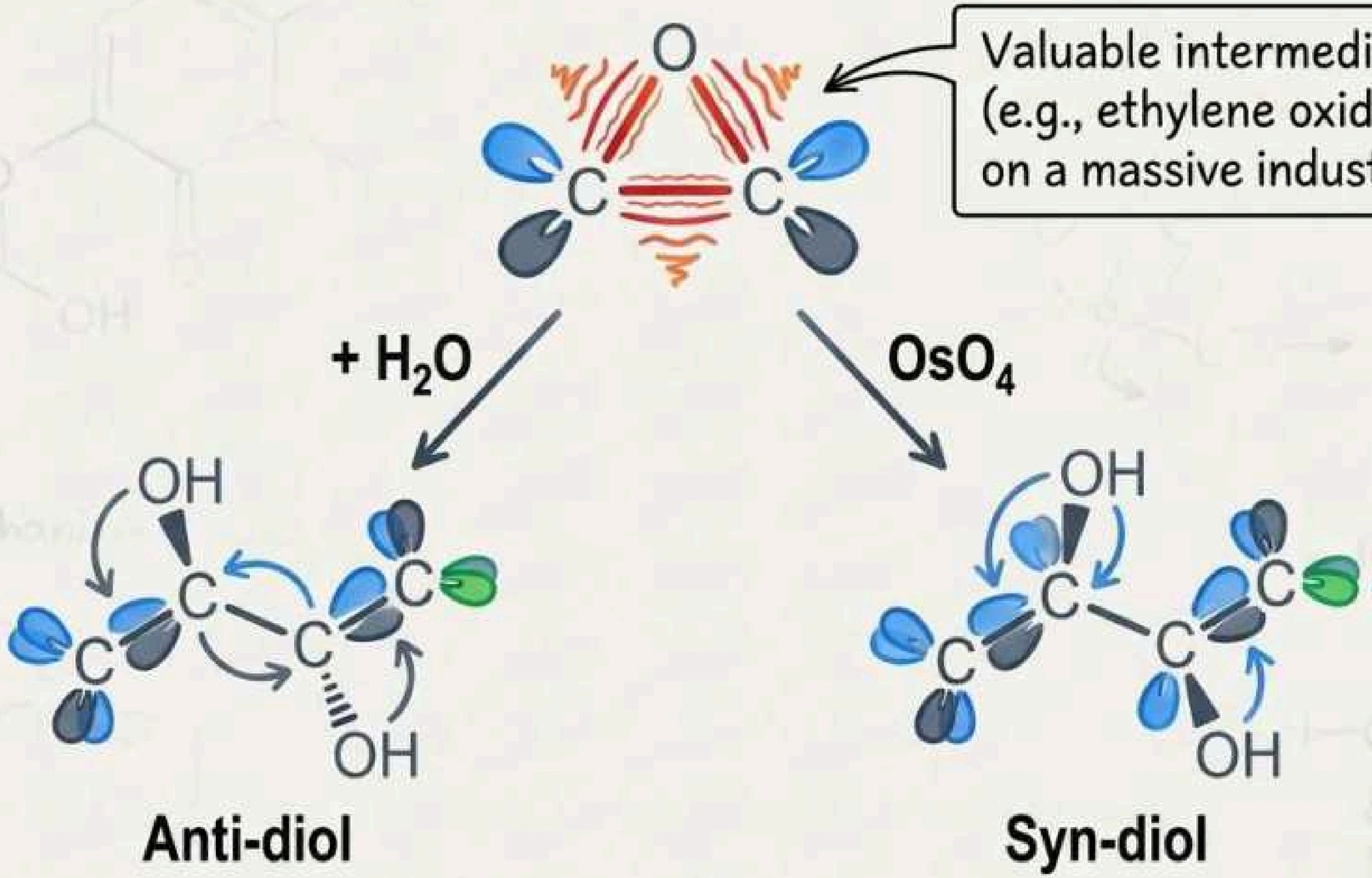


Releases ~120 kJ/mol
(Heat of Hydrogenation)

Measuring this heat reveals that more substituted alkenes are more stable.

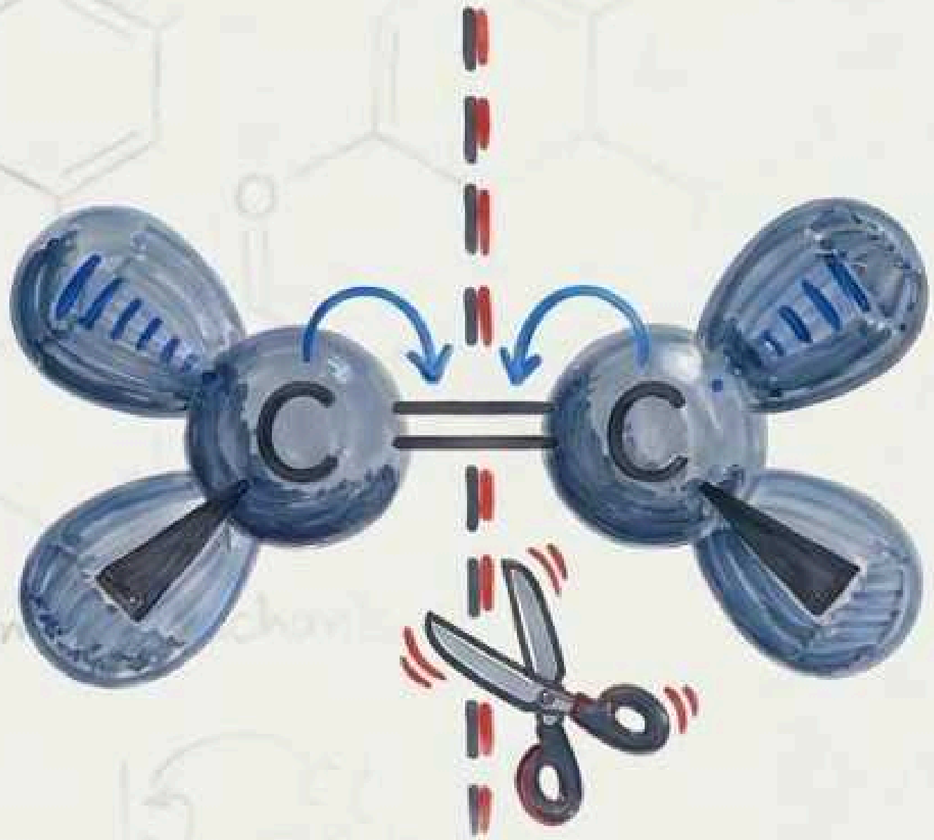
Peroxy acids form strained epoxides that open into specific diols

¶ 6.11

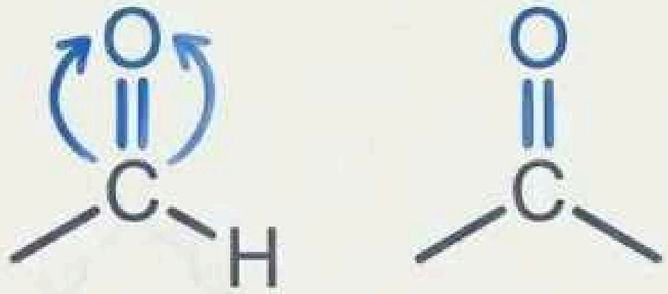


Oxidative cleavage breaks the carbon skeleton completely

¶ 6.12

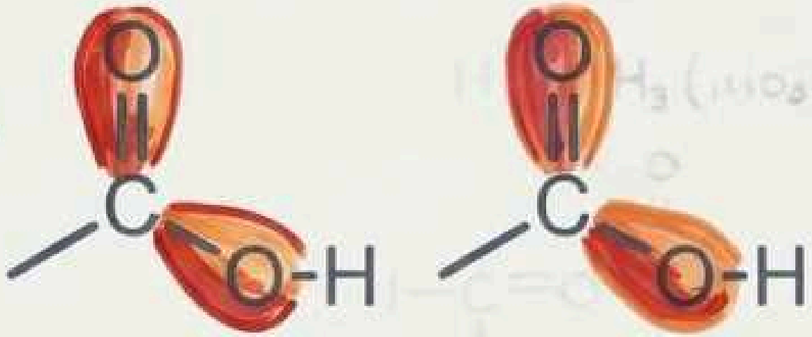


Ozonolysis
(O_3)



Aldehydes and Ketones

Hot
Permanganate
($KMnO_4$)

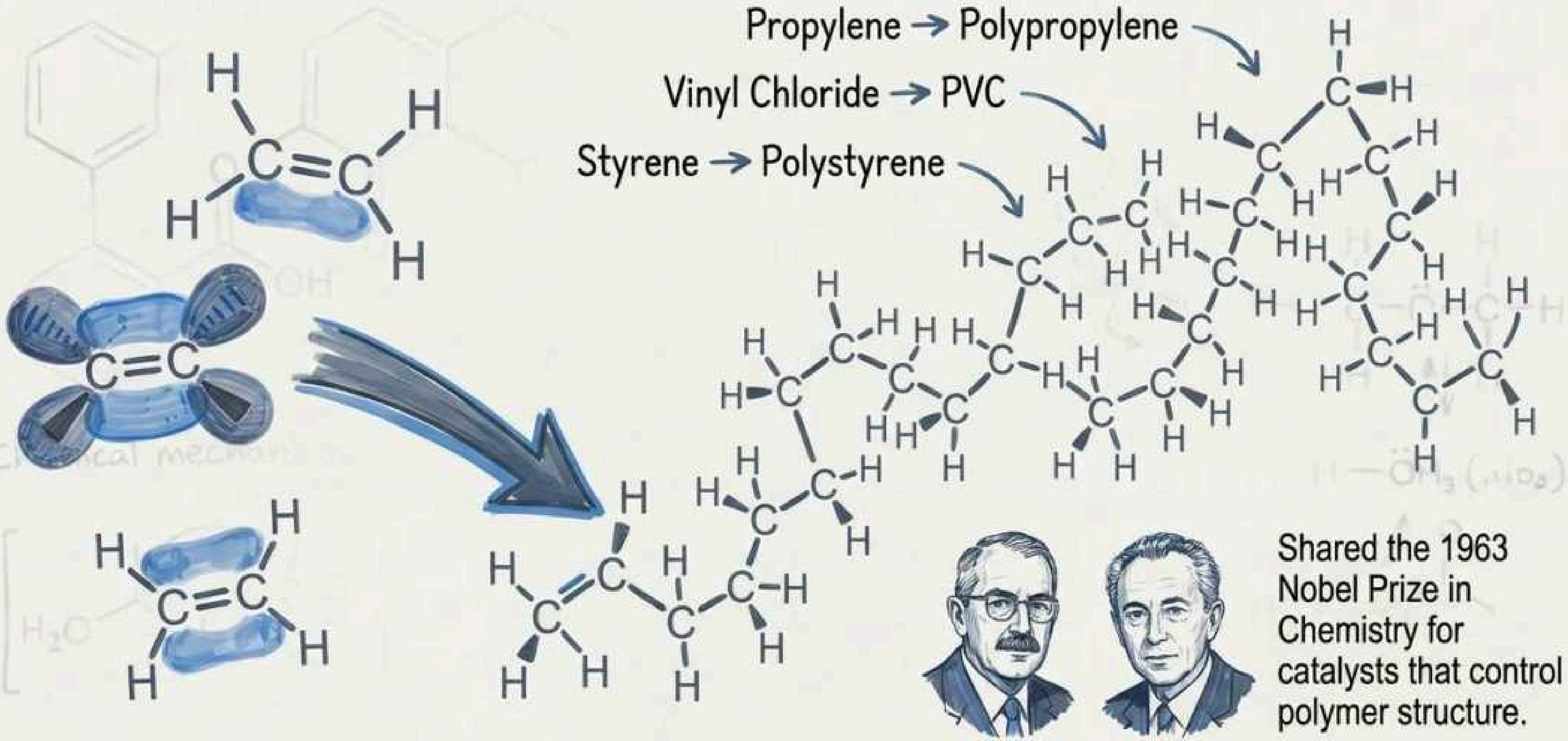


Carboxylic Acids

Historically used to deduce unknown alkene structures by identifying the shattered fragments.

Addition polymerization links monomers into industrial plastics

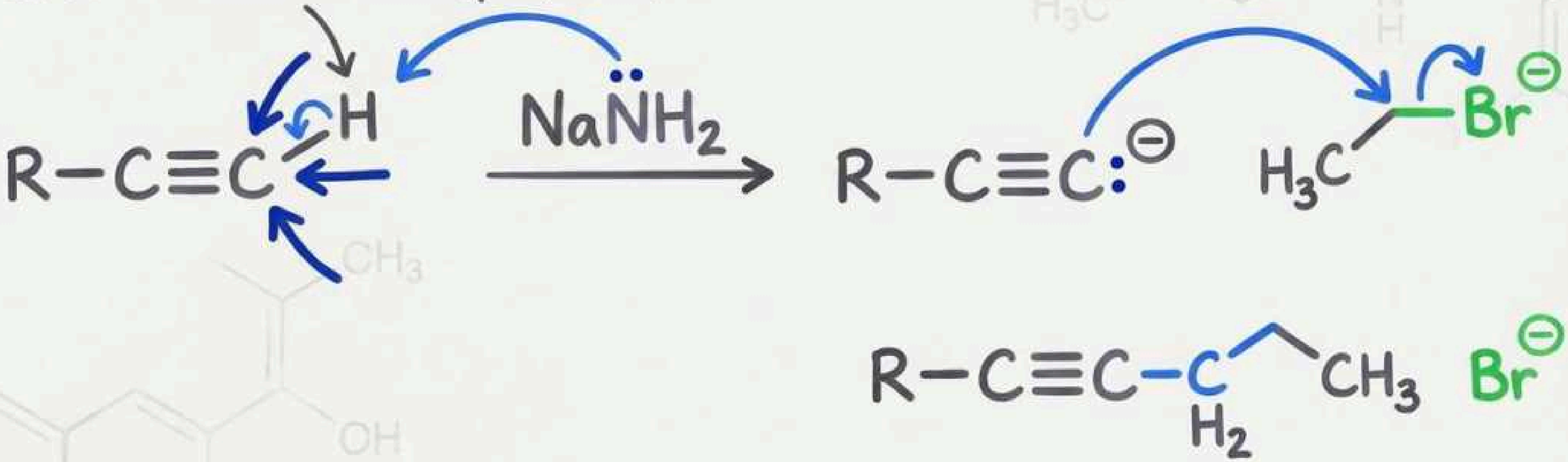
¶ 6.13



Shared the 1963 Nobel Prize in Chemistry for catalysts that control polymer structure.

Terminal alkynes act as carbon nucleophiles to build longer chains

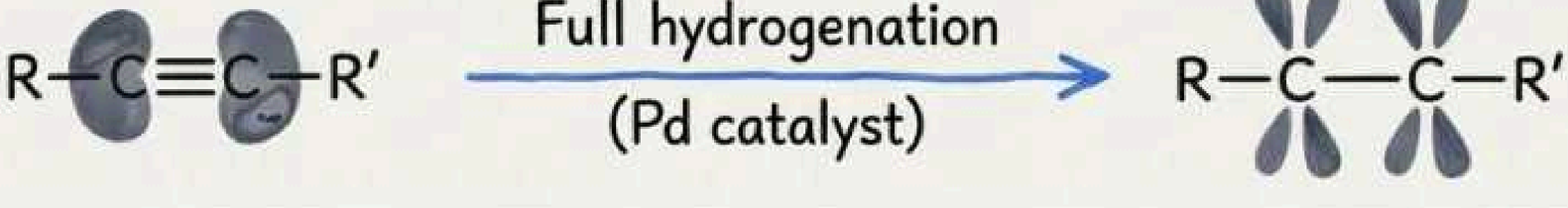
sp carbon holds electrons close → Acidic Proton ($pK_a \sim 25$)

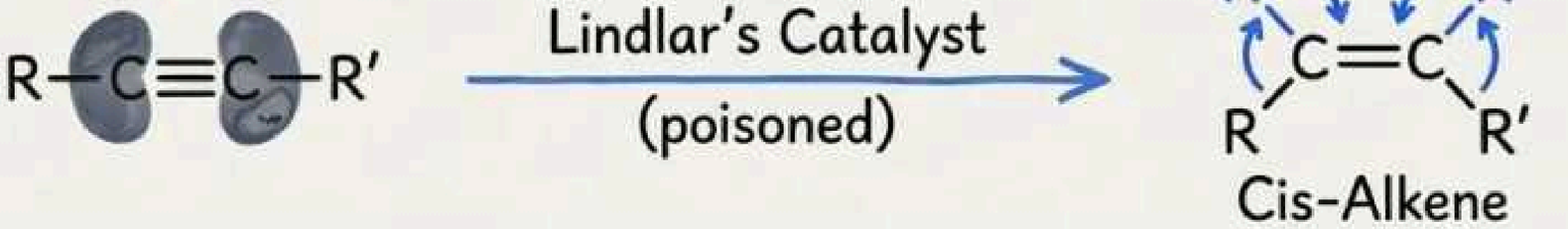


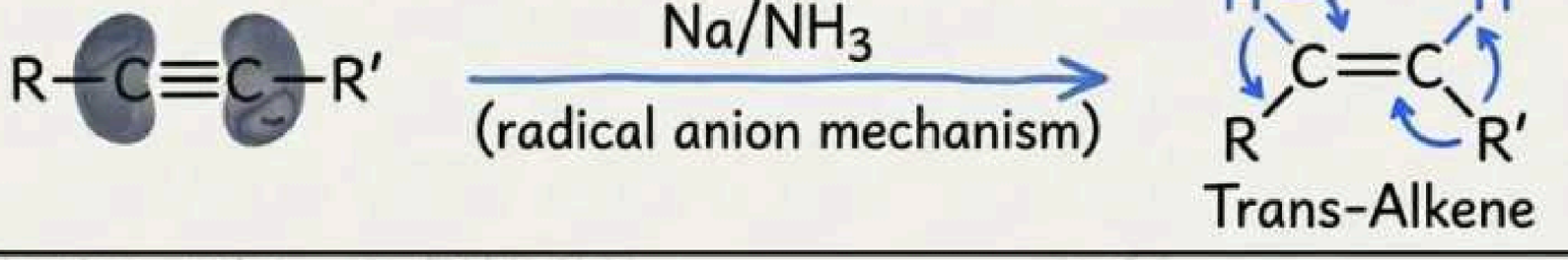
A key method for forging new Carbon-Carbon bonds.

Chemists control alkyne reduction to dictate double bond geometry

Alkyne Reduction Matrix

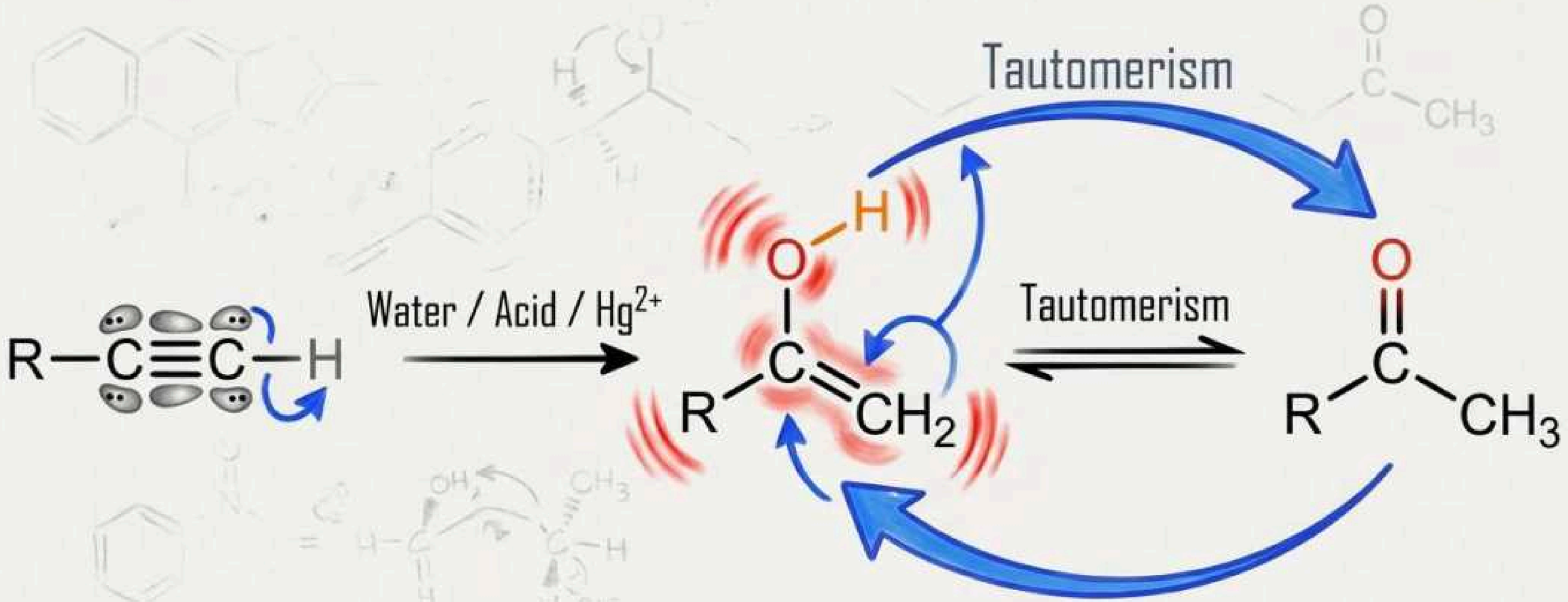






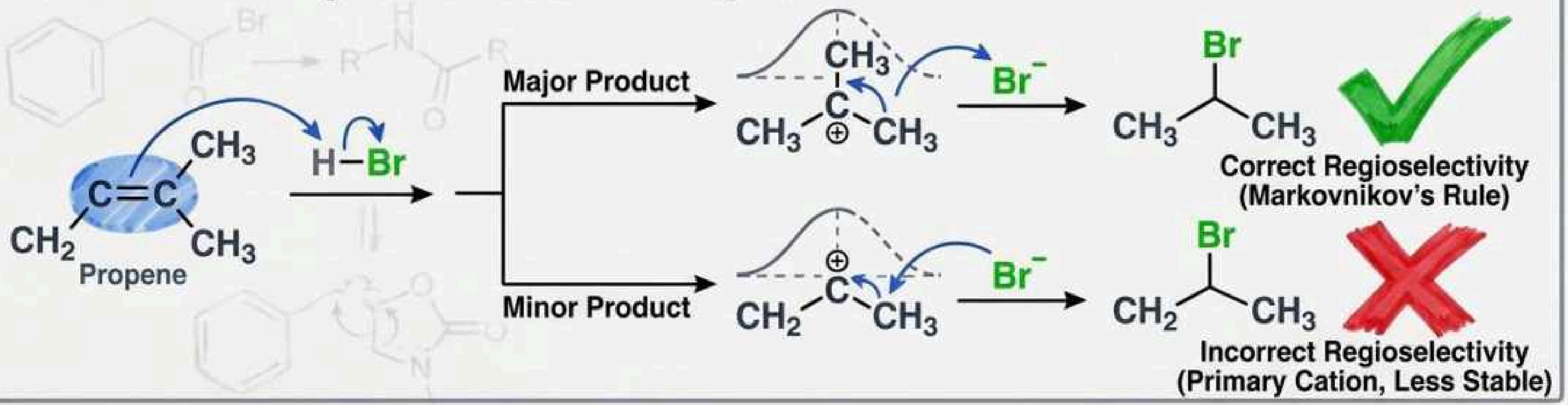
Alkyne hydration triggers tautomerism from unstable enols to stable ketones

¶ 6.16

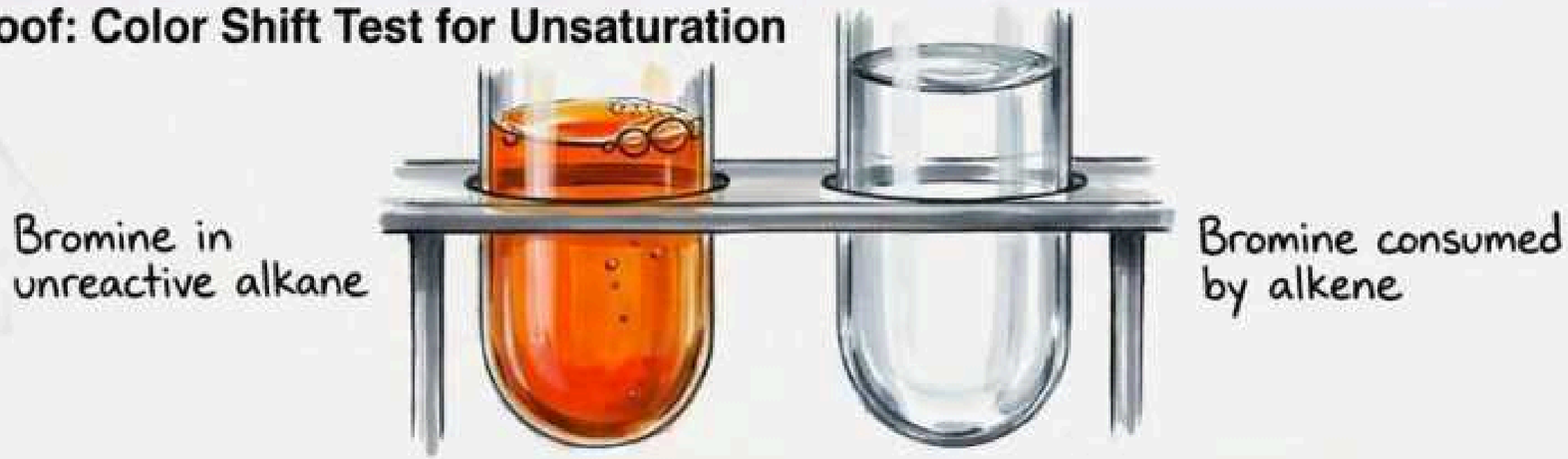


Hydroboration of a terminal alkyne shifts this process to yield an aldehyde instead. This bridges us to the carbonyl chemistry of Organic Chemistry II.

The Structural Proof: Regioselective Addition to Propene



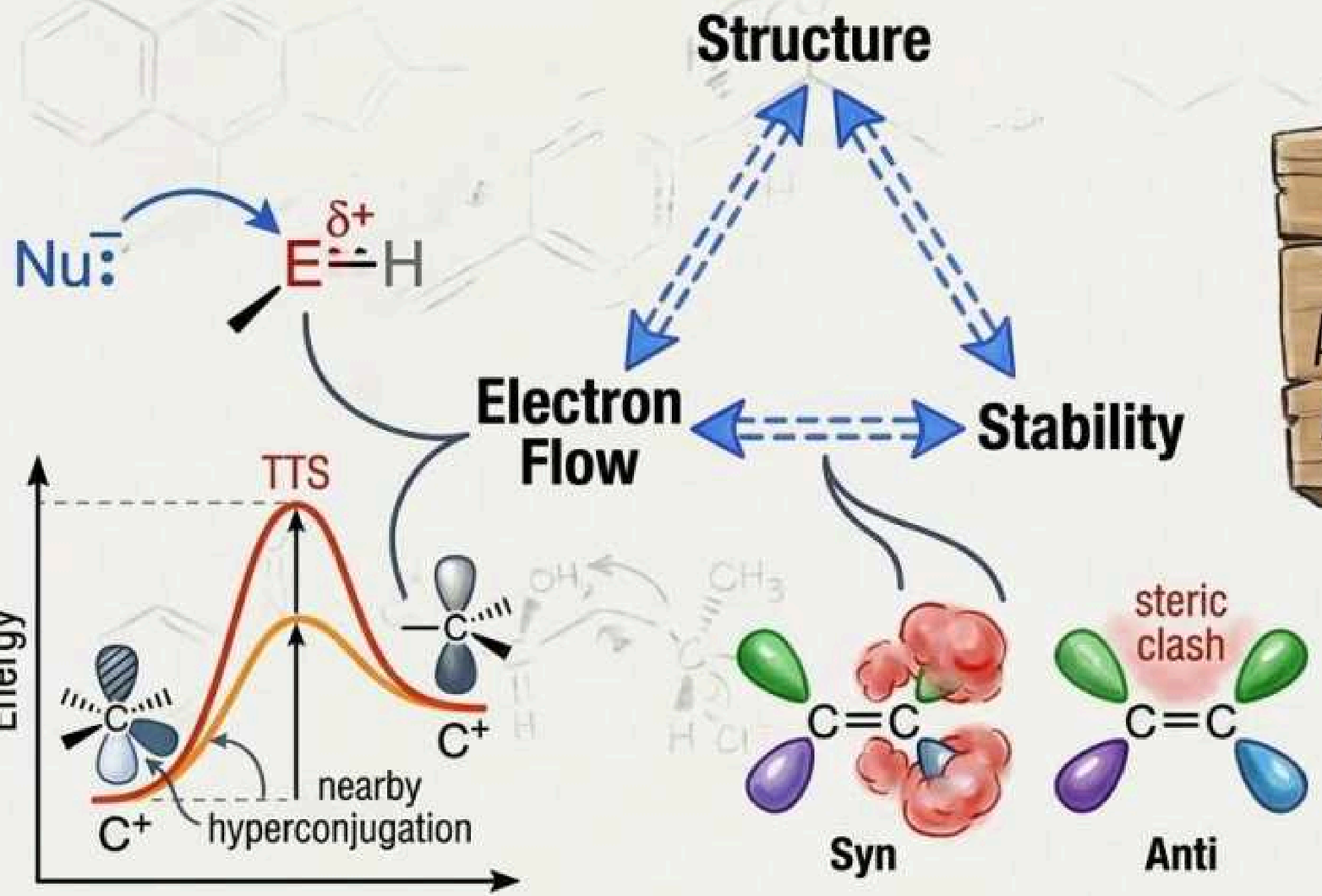
The Macroscopic Proof: Color Shift Test for Unsaturation



A simple test for unsaturation used long before modern instruments existed.

Structure, electron flow, and stability govern organic chemistry

¶ 6.18





A first course ends here.